

## Final Report

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### Project Title:

### **"LOW"-TEMPERATURE REACTIVITIES OF ULTRA-HIGH TEMPERATURE CERAMICS (Hf-X System)**

**Principal Investigator:** Dr. Yigal Blum  
**Institute:** SRI International  
**Address:** 333 Ravenswood Avenue, Menlo Park, CA 94025  
**AFOSR Contract Number:** F49620-03-C-0026  
**AFOSR Program Manager:** Dr. Joan Fuller

### Abstract

A growing interest in ultra-high temperature ceramics and their aerospace and turbine applications has led to a renewal of activities to fabricate  $\text{MB}_2/\text{SiC}$  composites as the materials of choice, because of their high thermal and oxidation resistance stability. Unfortunately, these composites are currently formed by an expensive, size and shape limited hot-press operation at a temperature range of 1900 to 2200°C.

The project investigated chemical reactions at and below 1500°C that can lead to structures and coatings consisting of monolithic  $\text{HfB}_2/\text{SiC}$  composite microstructures (and also  $\text{HfC}$ ,  $\text{ZrB}_2$ , and  $\text{ZrC}$  composites) under pressureless conditions. These can be employed in reactive and shape-forming processes in which ceramic precursors or reactive powders are employed. Special attention was paid to exothermic reactions and formers of in situ liquid phases, especially reactions involving elemental Hf and Si.

Substantial reactions between loosely mixed powders or between powders and reactive surfaces were detected by X-ray diffraction analyses, microstructural studies, and energy-dispersive X-ray spectroscopy. These findings confirmed significant reactivities starting at 700°C between Hf metal or its ceramic compounds. "Bulk" melting of Hf at external temperatures of 1100°C and higher (over 1000°C below its adiabatic melting point was observed in many of the reactions.

### Acknowledgment/Disclaimer

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## **"LOW"-TEMPERATURE REACTIVITIES OF ULTRA-HIGH TEMPERATURE CERAMICS (Hf-X System)**

### **Introduction**

A growing interest in ultra-high temperature ceramics (UHTCs, performing at temperatures above 1500°C) and their aerospace and turbine applications has led to a renewal of activities to fabricate MB<sub>2</sub>/SiC composites as the materials of choice because of their high thermal and oxidation resistance stability. The concept of these composites was established in the late 1960s, but work on these materials was discontinued, partly because of the extreme processing conditions, limited structural processing capability, and irreproducibility of these materials. These composites are formed by a hot-press operation at a temperature range of 1900 to 2200°C.

"Mild-temperature" (at and below 1500°C) chemical reactions that may lead to structures and coatings containing HfB<sub>2</sub>/SiC compositions under pressureless or mild-pressure conditions provide a promising approach for bypassing the extreme processing conditions and size and shape limitations of current hot-press processes. Such reactions are anticipated to be involved in reactive and shape-forming processes in which ceramic precursors or reactive powders are employed. Ceramic precursors in the form of polymeric materials are advantageous for processing of coatings and shapes via "polymer processing techniques," as well as for their potential to lower the phase development temperature. Reactive powders are expected to provide in situ exotherms that can locally enhance sinterability and development of the desired phases of the composites. Reactive powders, such as Hf, Si, C, B, and B<sub>4</sub>C, can also serve as interacting fillers with the preceramic polymer formulations.

In situ formation of the SiC phase was also evaluated as a practical approach in which a polymeric precursor to carbon (such as a phenolic resin) served initially as a binder to the other powder components and then reacted with molten silicon (reaction-bonded SiC), which was introduced either as a powder mixed in the original composite formulation or as a subsequent infiltrant that assisted the overall composite densification and mechanical characteristics. The carbon source can also serve as an in situ forming reagent for HfC.

This project paid special attention to exothermic reactions, as well as to formers of a liquid phase, especially reactions involving Hf metal. Both can aid the desired phase formation, microstructure development, and sintering of the composite under milder conditions than currently practiced.

### **Research Summary**

**Year 1.** In the first year the project focused on reactions between loosely mixed powders that have melting points significantly above 1500°C (except B<sub>2</sub>O<sub>3</sub>). Using X-ray diffraction (XRD) analyses, microstructural studies using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) techniques have confirmed the presence of unique reaction mechanisms between the loosely connected particles, especially related to the disappearance of the large Hf powder particles.

The **first year** studies consisted of the following:

1. A thorough literature search for relevant chemistry of Ti, Zr, and Hf compounds (borides, carbides, nitrides, and oxides)
2. An assessment of the results and development of a better understanding of the mechanisms of reactions leading to Hf compounds, especially  $\text{HfB}_2$ , at  $1500^\circ\text{C}$  or below
3. An assessment of the approaches to forming the SiC phase in the UHTC composite from precursors and Si metal at  $1500^\circ\text{C}$  or below
4. An initial evaluation of reactions between Hf and compounds containing B or C.

The reaction screening study revealed that the chemistry of as-received powders from the system Hf-B-C-N and Hf-B-Si-C-N is very rich and reactive, and even Hf-based ceramics are substantially reactive at temperatures below  $1500^\circ\text{C}$  in spite of their ultra-high melting temperature. These reactions are not expected to occur as solid-solid phase reactions in the absence of gaseous or liquid phase facilitation, especially when the contact surface between the reactants is minimal. Thermodynamically, such reactions are exothermic similarly to combustion synthesis and self-propagating high-temperature synthesis (SHS) and are anticipated in contrast to carbothermal reductions that are endothermic. However, the processing conditions provided in the current study were much different than those provided during the conventional SHS processes that cannot be easily quenched once they are ignited.

The different reaction pathways that are feasible in the Hf system at  $1500^\circ\text{C}$  and below are summarized in Figure 1.

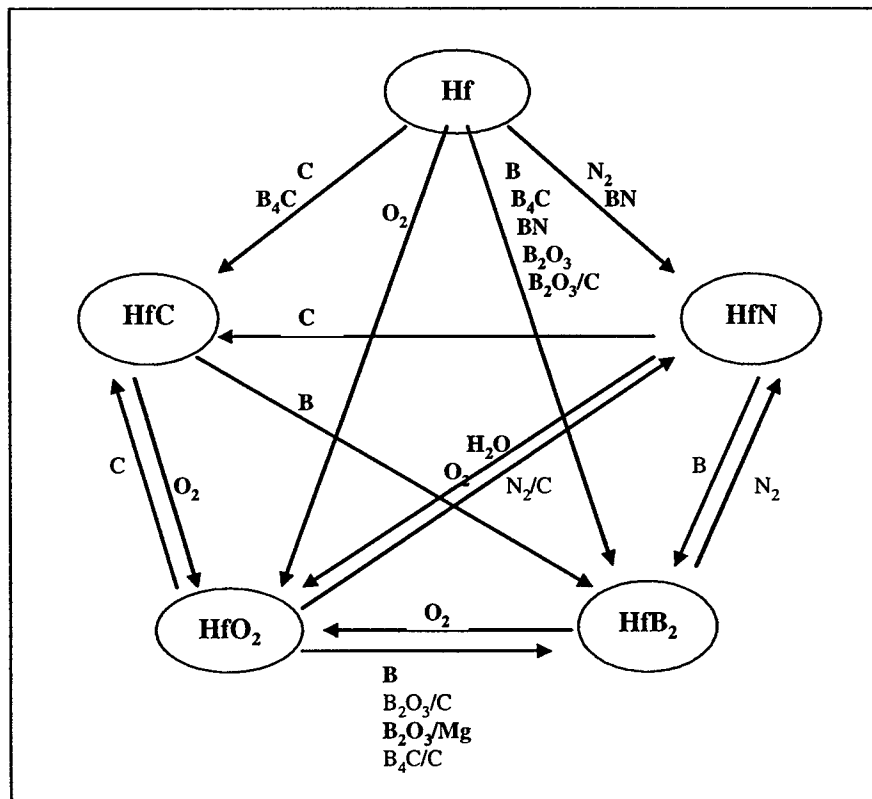


Figure 1: The chemistry in the Hf-X system that can proceed at temperatures below  $1500^\circ\text{C}$ .

Table 1 shows a series of reactions with Hf (primarily reactions forming  $\text{HfB}_2$ ) that are exothermic and evidently show significant reactivity at and below  $1500^\circ\text{C}$  according to XRD analysis. Numerous reactions with either elemental Hf or all of its derivatives were found to cause the formation of  $\text{HfB}_2$ . Of these, only the carbothermal and borothermic reactions may require temperatures higher than  $1500^\circ\text{C}$  to take place.

Table 1: Reactions between powder mixtures involving the presence of metallic Hf powders.

Reactants	Weight Change During Heating to $1500^\circ\text{C}$ (wt%)	Observed Crystalline Phases After Heating to $1500^\circ\text{C}$ (Found by XRD)
Hf + GP Phenolic (calculated for 3 equivalents of C)	-18.2	HfC (very strong) HfO <sub>2</sub> (weak)
Hf("3C") from AF-2 + $2\text{H}_3\text{BO}_3$ dissolved in water	-33.3	HfB <sub>2</sub> (very strong) HfO <sub>2</sub> (strong)
Hf + $\text{B}_2\text{O}_3$ + 3C ( via novolac pyrolysis)	-19.6	HfO <sub>2</sub> (very strong) HfB <sub>2</sub> (strong)
Hf + B	None	HfB <sub>2</sub> (very strong)
Hf + C (carbon black)	+1.2	HfC (very strong)
Hf + $\text{B}_2\text{O}_3$ + C (1h at $1500^\circ\text{C}$ )	-15.5	HfO <sub>2</sub> (very strong) HfB <sub>2</sub> (strong)
Hf + $\text{B}_2\text{O}_3$ + C (8h at $1500^\circ\text{C}$ )	-21.9	HfB <sub>2</sub> (very strong) HfC (strong) HfO <sub>2</sub> (medium)
Hf + $\text{B}_2\text{O}_3$	-9.1	HfO <sub>2</sub> (very strong) HfB <sub>2</sub> (strong)
Hf + 2BN	+1.3	HfN (very strong) $\text{Hf}_{55}\text{B}_{30}\text{N}_{10}$ (combined with the HfN picks) HfB <sub>2</sub> (medium) HfO <sub>2</sub> (weak) BN (weak)
Hf + $\text{B}_4\text{C}$	+0.1	HfB <sub>2</sub> (very strong) HfC (weak)

Table 2 summarizes other exothermic reactions of the Hf system that occur at  $1500^\circ\text{C}$  or below according to XRD analysis.

Table 2: Reactions involving Hf derivatives carried at 1500°C.

Reactants	Weight Change During Heating to 1500°C (wt%)	Observed Crystalline Phases after Heating to 1500°C (Found by XRD)
HfB <sub>2</sub> + N <sub>2</sub>	+8.2 (at 1400°C)	HfB <sub>2</sub> (Strong) HfN (medium) Hf <sub>7</sub> O <sub>8</sub> N <sub>4</sub> (weak)
Hf + N <sub>2</sub>	+5.7 (at 1200°C)	NA (dark golden color)
HfC + N <sub>2</sub>	No change	HfC (very strong)
HfC + 2B	-0.7	HfB <sub>2</sub> (very strong) HfC (strong)
HfN + 2B	No change	HfB <sub>2</sub> (very strong) HfN (weak)
HfN + C	+0.5	HfN (strong) HfC (weak)

An example for the phases developed in the Hf-B-Si-C system is presented in the XRD pattern shown in Figure 2. When powders of all the above elements are mixed at a stoichiometric ratio and reacted as loosely mixed powders, the only observed phases are the desired HfB<sub>2</sub> and SiC.

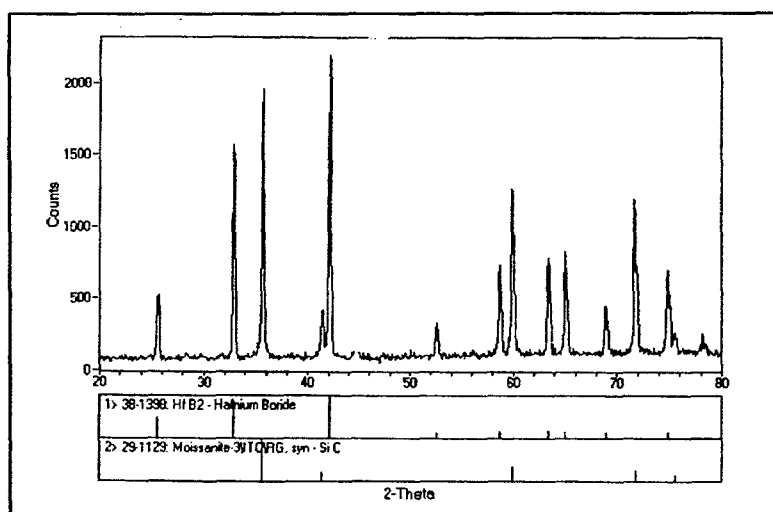


Figure 2: XRD pattern of the reaction between loosely mixed powders of Hf, B, Si and C in a stoichiometric ratio reveals the exclusive formation of micron-size phases of HfB<sub>2</sub> and SiC.

**Year 2.** In the second year the research focused on reactions between the surfaces of various substrates with loosely deposited powders of the materials mentioned above, in an attempt to assess solid versus liquid phase reactivities at 1500°C or below. In addition, a few reactions between bulk reagents with limited or loose interfaces were assessed.

Significant Hf metal melting incorporated with extensive chemical reactivity and product crystallization were clearly observed in experiments carried out at furnace temperatures lower than 1000°C below the melting point of Hf (2272°C).

Figure 3 represents several of the studied reactions between powders and surfaces that indicate significant melting activities of either Hf powder or plate combined with phase formation due to the reactions with either boron- or carbon-containing powders or surfaces.

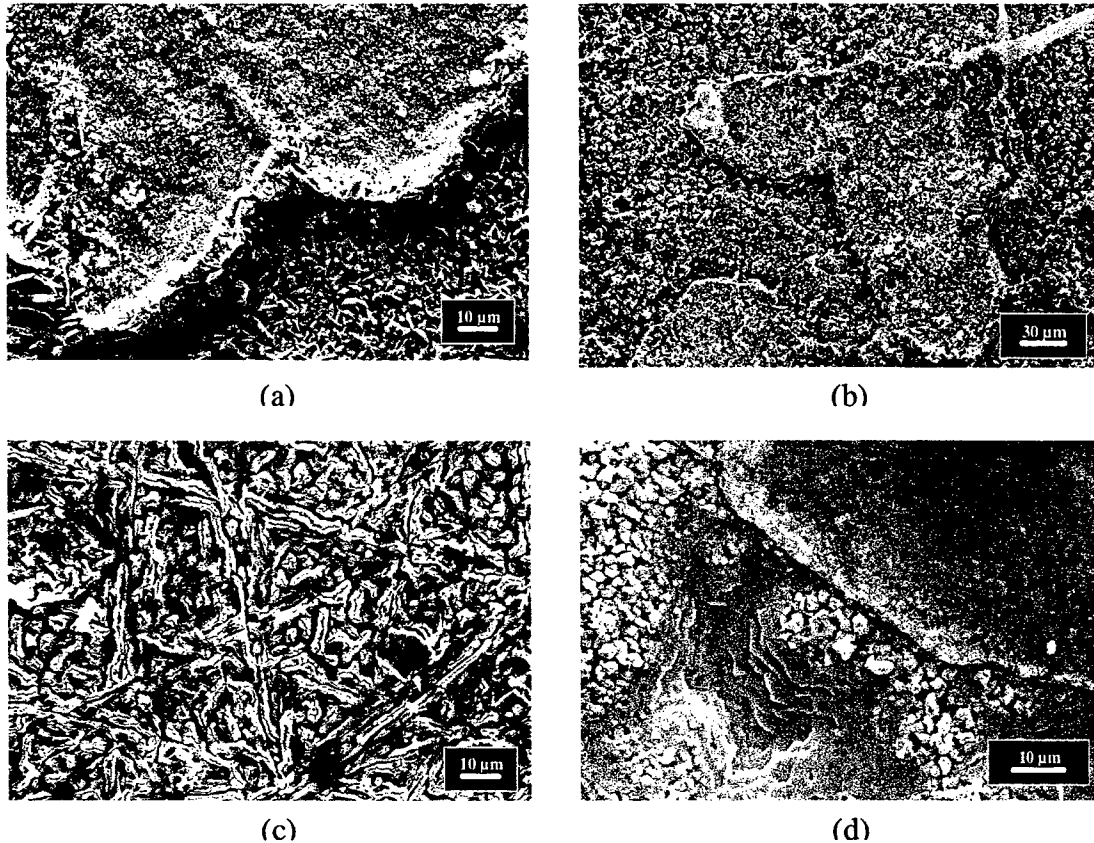
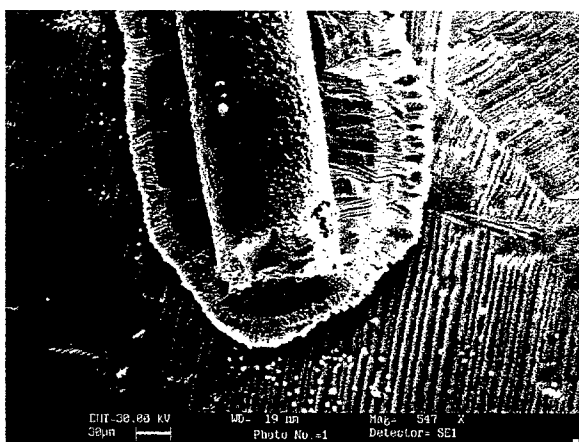


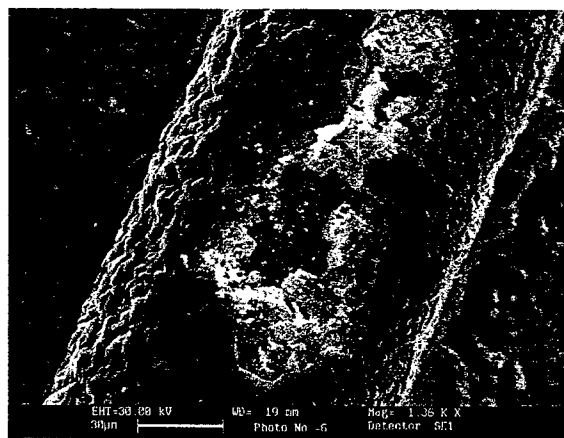
Figure 3: Evidence for melting at the surface of Hf plates during their reactions with powders containing B and/or C at 1500°C for 1 h. Reactions shown are with: (a) B powder, (b) B<sub>4</sub>C powder, (c) BN powder, and (d) carbon black powder.

Reactions can also occur between bulk materials such as boron monofilaments and Hf plates in which the initial contacting area between the two elements is very low. Observations included a dramatic formation of large crystallites caused by the interdiffusion of the materials to each other, with evidence of significant melt phenomena at the Hf plate but no melting of the boron monofilament. The monofilament had generated a microcrystalline structure in a reactive zone around the monofilament and become hollow due to the significant diffusivity of the B to the Hf area, as shown in Figure 4. Diffusion of Hf to the B monofilament has been detected too by EDS.

The work in Year 2 also included a limited assessment of reactions, phase development, and microstructure evolution of powders in the form of pressed pellets containing either polymeric precursors or reactive powders.



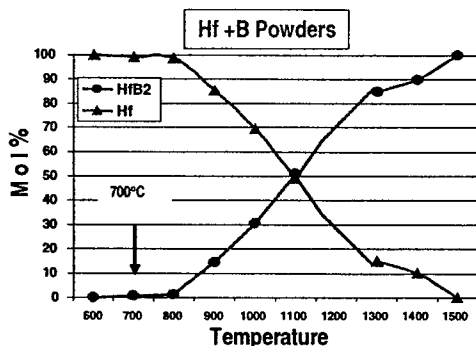
(a)



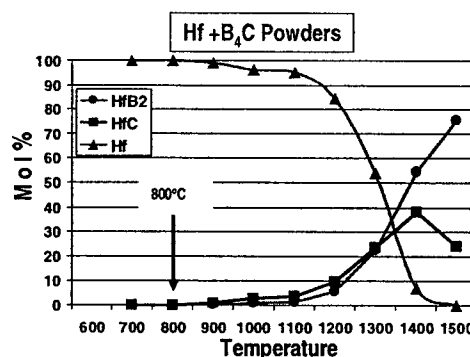
(b)

Figure 4: Strong heterogeneous interactions are observed between B monofilament and Hf plate at 1500°C, including: (a) Hf plate melting and recrystallization, formation of large  $\text{HfB}_2$  crystals obtained via diffusivity of B, and (b) the formation of an  $\text{HfB}_2$  hollow-shell template of the original B monofilament via diffusivity of the Hf into the boron phase.

**Year 3.** Several topics were assessed in the third year of the project. First, the threshold temperature and the progress of reactions between Hf and B, C,  $\text{B}_4\text{C}$ , or  $\text{B}_2\text{O}_3$  as a function of temperature were established. Threshold reactivities observed by the formation of crystalline products have been observed at temperatures as low as 700°C, as illustrated in Figure 5.



(a)



(b)

Figure 5: Plots of reaction progress as a function of temperature for: (a) mixed Hf and B powders and (b) Hf and  $\text{B}_4\text{C}$  powders.

The same reactions between powders of B and  $\text{B}_4\text{C}$  deposited at the surface of Hf film reveals the formation of a molten Hf phase at temperatures between 1100 and 1200°C, as illustrated in Figure 6.

In conjunction with a parallel AFOSR project led by Dr. Jochen Marschall, a mathematical and computational model was established. The model attempts to validate

the Hf melting phenomenon as a consequence of an exotherm-derived local heat accumulation that accelerates the SHS-like reactions. The model for the reaction at the interface between Hf and C indicates that at about 1200°C provided by external heat the interface temperature accelerates exponentially and reaches very quickly the adiabatic temperature.

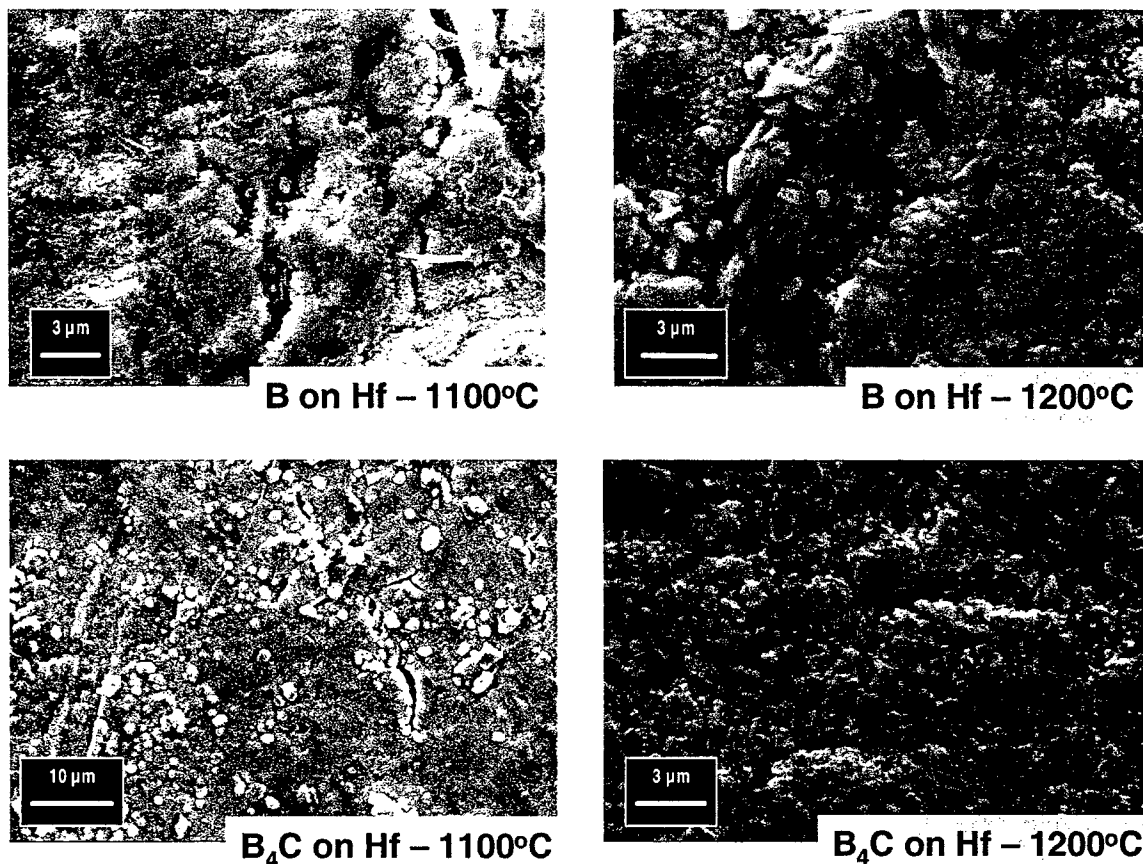


Figure 6: A molten phase of Hf is formed at temperatures between 1100 and 1200°C during the reactions of boron-containing powders loosely deposited at the surface of Hf films.

Another task in the third year assessed the phase and microstructure evolution inside uniaxially pressed pellets that were prepared from combinations of  $\text{HfB}_2$  and  $\text{SiC}$  precursors, including reactive powders and polymeric precursors. The pressed pellets were heat treated at 1500°C under atmospheric pressure or hot pressing conditions. No densification is obtained under pressureless conditions although major reactivity and phase transformation has occurred. In the hot press experiments, higher densification has been obtained for mixtures containing reactive powders rather than the final phase powders.

### Personnel Supported or Associated

The following researchers from SRI and elsewhere were involved in performing this project:

Dr. Yigal Blum (SRI)  
Dr. Marc Hornbostel (SRI)  
Dr. D. Brent MacQueen (SRI)

Program Manager, Chemistry of Materials Program  
Senior Materials Scientist, Materials Research Lab  
Senior Chemist, Chemistry of Materials Program

Mr. David Hui (SRI)  
Mr. Steve Young (SRI)  
Dr. Jochen Marschall (SRI)  
Dr. Esperanza Alvarez (SRI)  
Prof. Hans-Joachim Kleebe

Chemist, Chemistry of Materials Program  
Scientist, Molecular Physics Lab  
Senior Scientist, Molecular Physics Lab  
Senior Chemist, Chemistry of Materials Program  
Director of Electronic Microscopy Lab (Colorado  
School of Mines)

## Publications

1. Y. D. Blum and H-J. Kleebe, "Chemical Reactivities of Hafnium and its Derived Boride, Carbide and Nitride Compounds at Relatively Mild Temperatures," *J. Mater. Sci.* 39:6023-42, 2004.
2. A TEM picture of nano Hf compounds evolved at the surface of BN flake was published as the cover of the *J. Am. Ceram. Soc.*, January 2004.
3. Y. D. Blum, S. Young, and D. Hui, "Chemical Reactivity: In Search of Better Processing of  $\text{HfB}_2/\text{SiC}$  UHTC Composites," in *Composites, Ceramic Transactions*, 177, J. P. Singh, N. P. Bansal, B. G. Nair, T. Ohji, and A. de-A. Lopez, Eds., 103-114 (2005).
4. Yigal D. Blum, Steven Young, David Hui, and Esperanza Alvarez, Hafnium Reactivity Below  $1500^\circ\text{C}$ : In Search of Better Processing of  $\text{HfB}_2/\text{SiC}$  UHTC Composites, submitted to the proceedings of Cocoa Beach Meeting of the Am. Ceram. Soc. (January 2006).
5. Y. D. Blum, J. Marschall, and S. Young, "Mild-Temperature Incipient Melting of Hf During Interface Reactions with Boron and Carbon Containing Powders," manuscript in preparation.



## Interactions and Transitions

### 2003

1. Presentation at the AFOSR workshop for Ultra High Temperature Ceramics; November 5, 2003, Wintergreen, Virginia.

### 2004

2. Proposal to AFRL for applying the results of this project; i.e., for processing of UHTC coatings on C and SiC materials (March 2004).
3. Presentation at the American Ceramics Society Annual Meeting, April 20, 2004.
4. Collaborative effort with Prof. H.-J. Kleebe to study nanophase development during exothermic reactions with Hf and its compounds.
5. Series of discussions with the Thermal Protection Branch at NASA Ames about advanced processing of UHTC during 2004 (with Dr. S. Johnson, Dr. D. Elerby, Dr. Stackpoole).
6. Collaboration with Dr. Laurent Sibelle from NASA Huntsville in writing a NASA proposal for UHTC materials for missions to Titan and Neptune (2004).

7. Participation in the annual review meeting of AFOSR in Wintergreen, VA, August 16, 2004.
8. Presentation at the Aerospace Workshop in Dayton, OH, August 29, 2004.
9. Beginning to perform an AFRL project to develop UHTC protective coatings for SiC/SiC and C/SiC composites based on concepts assessed in this project (August 2004).
10. Discussions with Ceradyne on new processes for boron-containing ceramics (with Dr. Biljana Mikijelj) led to the processing and analysis of selected hot-pressed HfB<sub>2</sub>/SiC discs using in situ chemical reactivity.

## **2005**

11. Hot press experiments at Ceradyne
12. Presentation at the American Ceramics Society Annual Meeting, April 12, 2005.
13. Submission of a new AFOSR proposal to continue this effort.
14. Collaboration with Dr. Jochen Marschall, under Dr. Marschall's own AFOSR project and the above joint AFRL project, to develop a model and simulation explaining the incipient melting of Hf at temperatures below 1500°C (in 2005).
15. Participation in the annual review meeting of AFOSR in Sedona, AZ, August 17, 2005.
16. Presentation at the Pacific Rim ceramic Societies meeting in Maui, Hawaii, September 10, 2005.
17. Presentation at the Cocoa Beach Meeting of the American Ceramic Society, January, 24, 2006.
18. Discussions with Prof. Bridget R. Rogers, Vanderbilt University, Nashville, TN, about collaboration on a new AFOSR project beginning in 2006.

**Transitions.** The chemistry studied in this project was selected for award by AFRL as the cornerstone for developing UHTC protective coatings on SiC-based substrates and formulations suitable for UHTC matrices for fiber-reinforced ceramics. This award is currently a one-year project involving collaboration between Dr. Blum and Dr. Marschall from SRI and Prof. Kleebe from Colorado School of Mines.

## **New Discoveries**

All the new work has been openly discussed and reported because of the fundamental nature of this project. The discoveries were not filed as patents or invention disclosures. Instead, they were published in a series of articles and presented orally at national and international conferences.

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14. ABSTRACT A growing interest in ultra-high temperature ceramics and their aerospace and turbine applications has led to a renewal of activities to fabricate MB2/SiC composites as the materials of choice, because of their high thermal and oxidation resistance stability. Unfortunately, these composites are currently formed by an expensive, size and shape limited hot-press operation at a temperature range of 1900 to 2200°C. The project investigated chemical reactions at and below 1500°C that can lead to structures and coatings consisting of monolithic HfB2/SiC composite microstructures (and also HfC, ZrB2, and ZrC composites) under pressureless conditions. These can be employed in reactive and shape-forming processes in which ceramic precursors or reactive powders are employed. Special attention was paid to exothermic reactions and formers of in situ liquid phases, especially reactions involving elemental Hf and Si. Substantial reactions between loosely mixed powders or between powders and reactive surfaces were detected by X-ray diffraction analyses, microstructural studies, and energy-dispersive X-ray spectroscopy. These findings confirmed significant reactivities starting at 700°C between Hf metal or its ceramic compounds. "Bulk" melting of Hf at external temperatures of 1100°C and higher (over 1000°C below its adiabatic melting point) was observed in many of the reactions.					
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